

SPECIAL COLLECTION: MECHANISMS, RATES, AND TIMESCALES OF GEOCHEMICAL TRANSPORT PROCESSES IN THE CRUST AND MANTLE

Ankerite grains with dolomite cores: A diffusion chronometer for low- to medium-grade regionally metamorphosed clastic sediments†

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ABSTRACT

Ankerite grains with dolomite cores occur in marls, pelites, and psammites from a Buchan terrain in Maine and a Barrovian terrain in Vermont (U.S.A.). Dolomite cores are typically ≤ 20 μm in diameter, have sharp but irregular contacts with ankerite, and have the same crystallographic orientation as ankerite rims. Ankerite grains with dolomite cores are common in the chlorite zone, less abundant in the biotite and garnet zones, and rare (Vermont) or absent (Maine) at higher grades. The texture and crystallographic orientation of dolomite and ankerite and the sharpness of the dolomite-ankerite contact are consistent with partial replacement of detrital dolomite by ankerite by solution-reprecipitation. Metamorphic biotite is in Fe-Mg exchange equilibrium with ankerite rims but not with dolomite cores, implying that ankerite did not form long after biotite (biotite has no phlogopite cores). Possible sources of iron for the formation of ankerite are reduction of ferric iron hydroxide or the smectite-to-illite reaction during diagenesis.

The sharpness of the dolomite-ankerite contact is a diffusion chronometer that constrains timescales of metamorphic process. Relatively low spatial resolution analyses of Fe/Mg across the contact with a NanoSIMS instrument and a FEG TEM give upper bounds on the thickness of the transition from ankerite to dolomite of ~ 2 and ~ 0.5 μm , respectively. Higher resolution analysis of BSE grayscale contrast with a FEG SEM gives a thickness ~ 100 nm. Fit of the grayscale profile to a model of one-dimensional diffusion across an infinite plane gives $Dt = 10^{-15}$ m^2 (\pm a factor of 5), where D is the effective Fe-Mg interdiffusion coefficient and t is the duration of diffusion. Using the published experimental determination of D , upper bounds on the residence time of ankerite grains with dolomite cores at peak $T = 400$ – 500 $^{\circ}\text{C}$, on the duration of linear cooling from peak T to 100 $^{\circ}\text{C}$, and on the duration of linear heating from 100 $^{\circ}\text{C}$ to peak T followed by linear cooling to 100 $^{\circ}\text{C}$ are all < 1 yr. For linear heating and cooling lasting 10^6 years, peak T could not have been > 100 $^{\circ}\text{C}$.

The question is what explains the occurrence of ultrasteepest composition gradients between dolomite and ankerite. Regional metamorphism on a timescale of a year or less is unrealistic. No barrier to diffusion at the dolomite-ankerite contact was observed in TEM images. Post-metamorphic formation of ankerite at very low temperature is ruled out by Fe-Mg exchange equilibrium between biotite and ankerite but not dolomite. It is unlikely that the steep composition gradients were preserved by intracrystalline pressure gradients.

Alternatively, the steep composition gradients would be consistent with timescales of metamorphic process $\sim 10^6$ years or longer if D values during metamorphism were approximately six orders of magnitude or more smaller than those measured in the laboratory. The error of measurement is much less, approximately \pm a factor of 2. A correction to D for the difference in P between measurements (0.1 MPa) and metamorphism (350–800 MPa) is likely an order of magnitude or less. Oxygen activity (a_{O_2}), however, was 17–20 orders of magnitude larger during the laboratory measurements than during metamorphism. A correction to measured D for the difference in a_{O_2} between experiment and metamorphism appears to be the likeliest way to reconcile the steep composition gradients with realistic timescales of metamorphism. Before ankerite grains with dolomite cores are fully realized as a useful diffusion chronometer for low- and medium-grade metamorphic rocks, the rates of Fe-Mg interdiffusion in ankerite and dolomite need to be calibrated as a function of a_{O_2} .

Keywords: Regional metamorphism, chemical diffusion, timescales of metamorphism, diffusion chronometry, transmission electron microscopy, NanoSIMS analysis